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Photochemical behaviour of a discoid, cinnamoyl-substituted azacrown derivative

Isomerization and crosslinking in the ordered state

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The photochemistry of a discoid, mesogenic hexa-cinnamoyl-substituted hexacyclen, which is mainly determined by the competition between E/Z-photoisomerization and (2 + 2)-photocycloaddition, is investigated in solution and in bulk. In a poor solvent, such as cyclohexane, columnar aggregates are supposed to be formed, due to the amphiphilic structure of the hexacyclen. Upon irradiation, these preformed aggregates undergo intracolumnar photocycloaddition between the photoreactive sites of the adjacent molecules. In the columnar mesophase, the liquid-crystalline order is disturbed by the E/Z-photoisomerization. It turns out that a highly fluid-like environment, which is present in aggregates formed in a poor solvent, is important to provide the required population of reactive sites in order to obtain a defined photocycloaddition reaction.

1. Introduction

In addition to the classical rod-shaped molecules which generate *calamitic* mesophases, disc-shaped molecules also form thermotropic liquid crystals [1]. These molecules usually consist of a central rigid core with six or eight laterally attached alkyl chains. As the central core, aromatic, metal-containing and metal-free heteroaromatic [2, 3] or alicyclic moieties [4] have been used. The mesophases generated are denoted by the term *discotic* and may either be nematic (N_D), where the only order is the parallel orientation of the short molecular axes, or columnar (D), where the discs are additionally stacked in columns, which are in turn placed in a regular array. Columnar mesophases were classified according to the symmetry of the lattice (hexagonal: D_h, rectangular: D_r, oblique: D_{ob}) and the order (e.g. D_{ho}) or disorder (e.g. D_{hd}) within the columns (see scheme 1) [2, 3]. According to recent investigations, cyclic oligoamines (e.g. the hexacyclen: 1,4,7,10,13,16-hexaazacyclooctadecane) also exhibit discotic columnar mesomorphism when acylated with suitable aromatic carboxylic acid derivatives [5, 6, 33]. These mesophases were assigned to D_{hd}, and the term tubular mesophase was proposed [5] because the macrocyclic units, stacked on top of one another, are expected to form hollow columns (see scheme 2).

In recent years, different methods have been employed in order to stabilize the columnar order. These include fixation of monofunctional disc-like mesogens on a polymeric backbone via flexible spacer units, polycondensation of bifunctional disc-like mesogens to main chain polymers [7, 9], and electron donor–acceptor interactions between electron withdrawing π-systems and monomeric, as well as polymeric, disc-like

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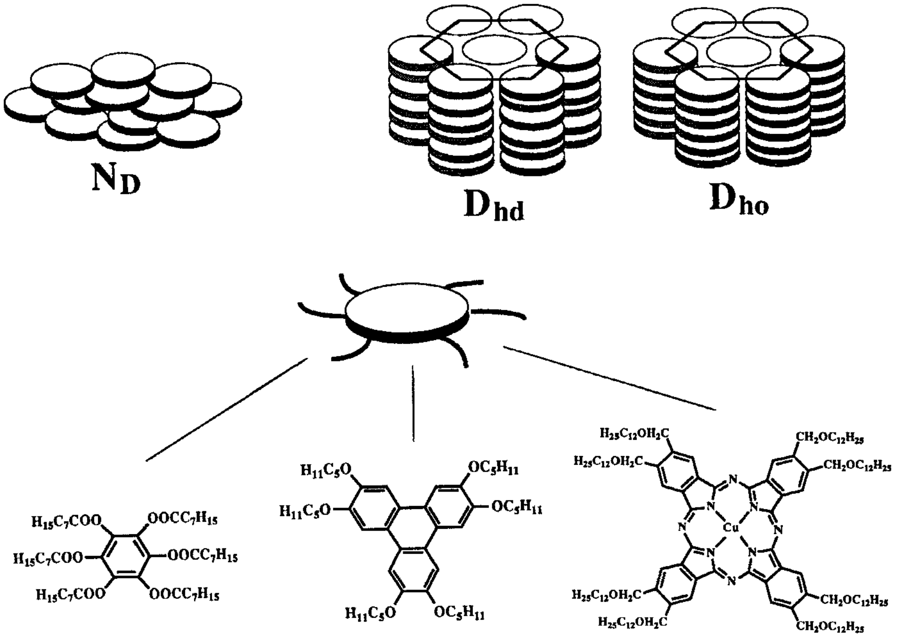
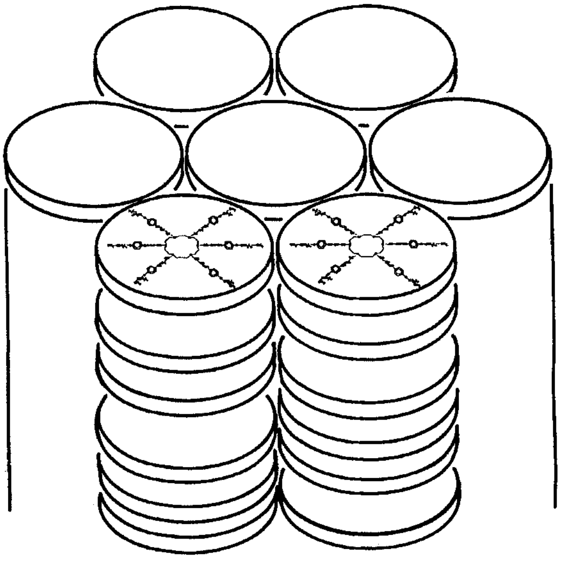
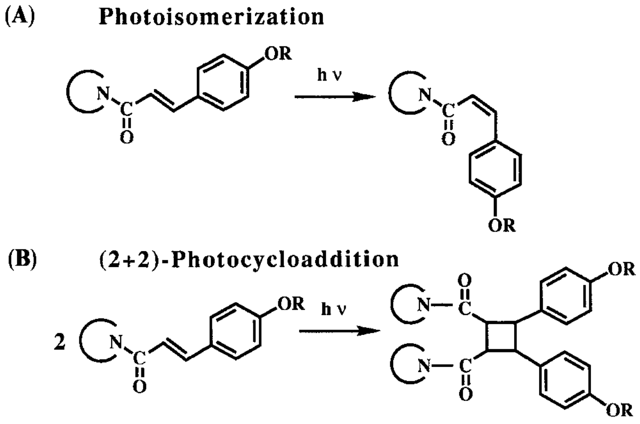


Scheme 1. Discotic mesophases: N_D = discotic nematic mesophase, D_{hd} = discotic hexagonal disordered columnar mesophase, D_{ho} = discotic hexagonal ordered columnar mesophase.



Scheme 2. Schematic representation of the D_{hd} mesophase.

electron donating π-systems [10]. The synthesis of polymers having cofacially arrayed discoid subunits has also attracted attention, because they may offer the possibility of producing low dimensional conductive materials, which could lead to interesting technological applications. The polycondensation of dihydroxy- and dichlorosiliconephtalocyanines, for example, leads to columnar poly(oxysiliconephtalocyanines) [11, 12]. The functionalization of a discotic columnar hexacyclen derivative has

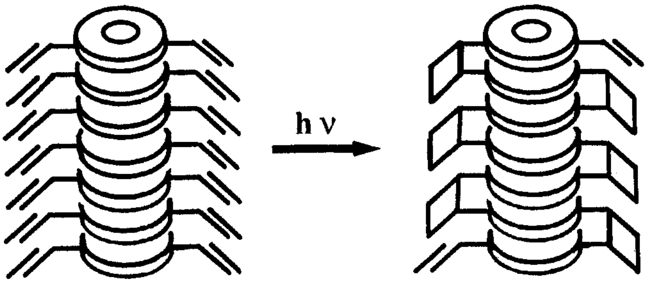


Scheme 3. Photoreactions of cinnamates.

already been realized via the introduction of laterally attached cinnamoyl substituents [6], which undergo photodimerization upon irradiation with UV light. In 1982, Billard *et al.* reported on a discotic triphenylen derivative substituted with cinnamoyl groups [13]. However, the corresponding mesophase belongs to the less ordered nematic type, as revealed by miscibility experiments and the optical textures.

The efficiency, selectivity and stereospecificity of mono and bimolecular photochemical processes can be influenced by the order and the mobility within a system [14–16]. The two extreme cases are exemplified, on the one hand, by the crystalline state, which exhibits a high degree of order and restricts the rotational and translational motion of the constituent molecules, and on the other hand, by the isotropic liquid state, which shows a low degree of order and high motional freedom. Both properties are combined to different extents in the mesophases of thermotropic liquid crystals and other ordered systems such as monolayers, liposomes, and membranes [14–17].

The (2 + 2)-photocycloaddition of cinnamic acid in its crystalline state is one of the oldest and best known reactions in solid state photochemistry [18]. The photoreaction is controlled by the crystal lattice (topochemical principle) and may be drastically altered by small changes in geometry [19]. The crystal structures of the reactants determine the course of the photocycloaddition according to their intermolecular distance and their orientation within the crystal. The topochemical principle thus leads to the preferred reaction route, whereby the deformation of the surface of the reaction cavity is minimized [20]. The reaction cavity is the space, of distinct size and shape, which the molecule occupies in the crystal lattice before the reaction. In solution E-cinnamic acid derivatives isomerize to the Z-form upon irradiation (see scheme 3 A). This transformation takes place until a photostationary state is reached [21]. Experimental results demonstrate that the (2 + 2)-photocycloaddition (see scheme 3 B) may also occur as a parallel proceeding reaction, leading to different stereo isomers of truxinic and truxillic acid. The formation of these derivatives is determined by the distribution of the reactive chromophore sites within the isotropic liquid or amorphous sample [22]. Photoisomerization and photocycloaddition of cinnamic acid derivatives have also been investigated in the ordered, fluid-like environment of different calamitic mesophases [16, 23–26]. The efficiency and regioselectivity of the photocycloaddition of cinnamic acid esters, for example, is significantly influenced by smectic mesophases [24, 25]. For cinnamic acid derivatives exhibiting calamatic mesomorphism due to



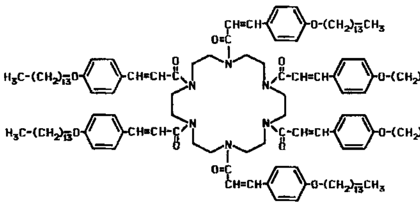
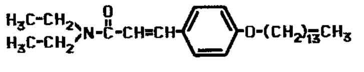
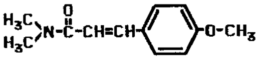
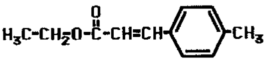
Scheme 4. Schematic representation of intracolumnar crosslinking in the columnar ordered state.

their molecular shape, it has been shown that only the trans isomer leads to the formation of mesophases [27]. Furthermore, it was claimed that (2 + 2)-photocycloaddition between a molecule in its excited state and its counterpart in the ground state proceeds via the trans configurated isomers [19].

Until now, the photoinduced variation of the geometrical shape and its influence on a columnar ordered discotic mesophase has not been studied. Here the (2 + 2)-photocycloaddition of discotic hexa-*N*-cinnamoyl-hexacyclen is presented as an alternative approach to stabilize the columnar order (see scheme 4). For this purpose the photoreaction was performed in both solution and the mesophase.

2. Experimental procedure

In order to elucidate the complex photochemistry of multifunctional hexacyclen **1**, several monofunctional model compounds (**2**, **3**, **4**) were investigated. The phase behaviour of all these cinnamates is summarized in the table. The synthesis and

1		C 217°C D_{hd} 233°C I
2		C 52-54°C I
3		C 101°C I
4		C 48°C I

C = crystalline
I = isotropic
D_{hd} = Discotic-hexagonal-disordered

Phase behaviour of the cinnamates investigated.

characterization of hexacyclen **1** has already been described [6]. Model compounds (**2, 3, 4**) were synthesized according to this description and to general procedures given in the literature. Irradiation experiments were performed using a 200 W high pressure mercury lamp as a light source in combination, either with an interference (296 nm, 313 nm), or a cut-off filter (WG 305). Light intensities were determined as 2 mW/cm^2 and 470 mW/cm^2 with interference (313 nm) and cut-off filters, respectively. A magnetic stirrer was used in order to obtain a homogeneous solution in those cases, when dissolved samples were irradiated. Thin films of hexacyclen **1** in the supercooled mesomorphic state were prepared between two quartz slides by radidly heating the sample into the isotropic melt and subsequently cooling it into the mesophase (220°C). At this temperature, the sample was sheared by moving the slides against each other in one direction. Subsequent annealing at 220°C and rapid cooling to room temperature led to a thin birefringent film, which was stable for several hours before recrystallization occurred. Annealing at high temperatures was generally carried out in an argon or a nitrogen atmosphere in order to prevent thermal decomposition. The photochemistry of the cinnamates was followed by UV (Perkin–Elmer Lambda 5), FT-IR (Nicolet 5 DXC), and ^{1}H NMR spectroscopy (400 MHz; Bruker Aspect 2000), and GPC chromatography (Waters; eluent: distilled chloroform + 0·5 vol% ethanol, UV-detection: 254 nm). Data obtained by GPC were analysed by a data module (Waters 745) using a polystyrene standard.

2.1. *Photoreactions in solution*

The competition between E/Z-photoisomerization and (2 + 2)-photocycloaddition in solution is illustrated in figure 1, where the decreasing extinction of hexacyclen **1** in

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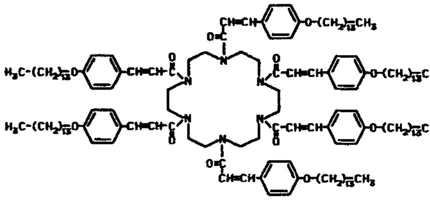


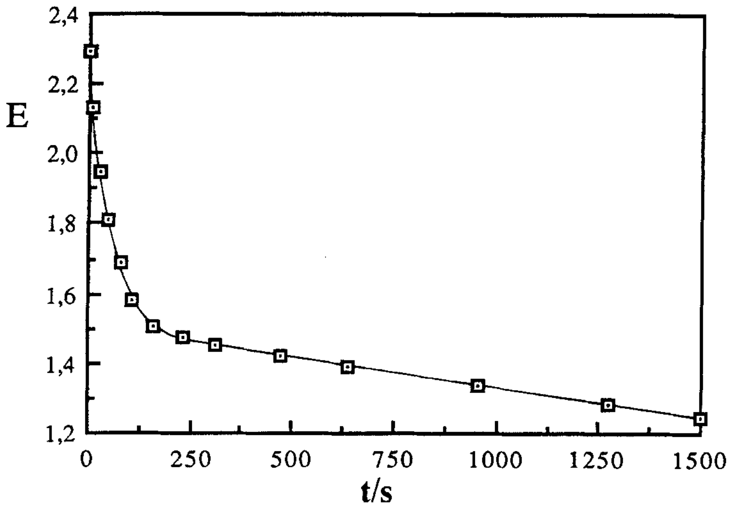


Figure 1. Irradiation of hexacyclen **1** in cyclohexane ($c = 10^{-5}$ mol/l); extinction at λ of 310 nm as a function of the irradiation time.

cyclohexane at λ of 310 nm is plotted versus the irradiation time. The UV spectra of the corresponding photolysis, from which this plot was derived, are given in figure 4. In figure 1 it can be seen that two different time scale processes occur. The first part exhibits a steep slope, whereas the second part shows only a moderate one. Photoisomerization and photocycloaddition are parallel proceeding reactions, but the large difference in the quantum yields causes the latter to proceed as a secondary event. Thus, in the relatively dilute system investigated, the first process (i.e. the fast one) can be ascribed to the E/Z-isomerization (see § 2.1.1.). On further irradiation a quasistationary state is established between the geometric isomers. Subsequently, the photocycloaddition (i.e. the slow process), which was only a minor parallel reaction in the beginning, starts to be significant and gives rise to oligomeric photoproducts (see §2.1.2.). It should be mentioned here that the model cinnamide **2** exhibits the same photochemical behaviour in dilute solution, than the one established for hexacyclen **1** (see figure 1).

The extent to which photoisomerization occurs relative to photocycloaddition is essential in regard to the desired intracolumnar crosslinking of azacrowns in their supramolecular arrangement. Photoisomerization can disturb the order within the system [27], whereas photocycloaddition should act as a tool to stabilize the columnar order. With the intention to determine the extent of each process, the uniformity of the photolysis was studied. In other words, the roles of photoisomerization and photocycloaddition, as well as other interferring side reactions, were investigated.

2.1.1. *Photoisomerization*

The optical absorption spectra of short time irradiated *N*-diethyl cinnamide **2** in cyclohexane are shown in figure 2. Three isosbestic points can be clearly observed, which indicates that E/Z-photoisomerization is the dominant process. The absorption bands of the E isomer at 310 nm, 292 nm and 282 nm decrease and a new absorption

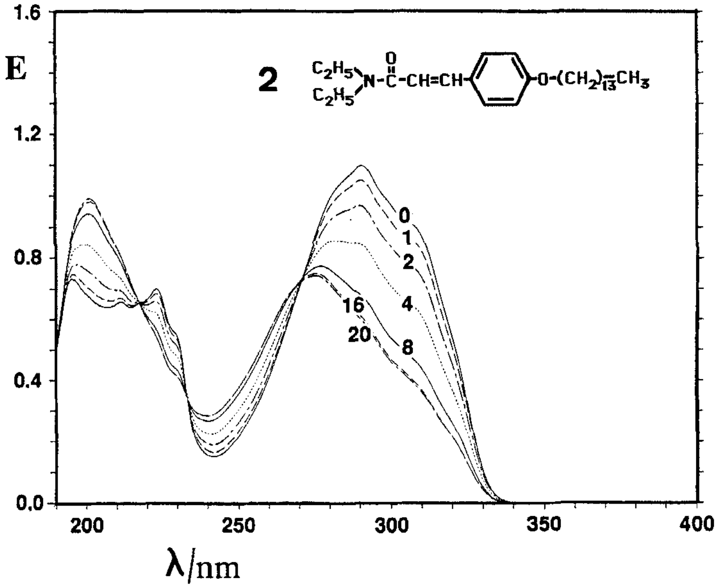


Figure 2. UV absorption spectra of short time irradiated *N*-diethyl-cinnamide **2** in cyclohexane ($c = 6 \times 10^{-5}$ mol/l); irradiation time in seconds.

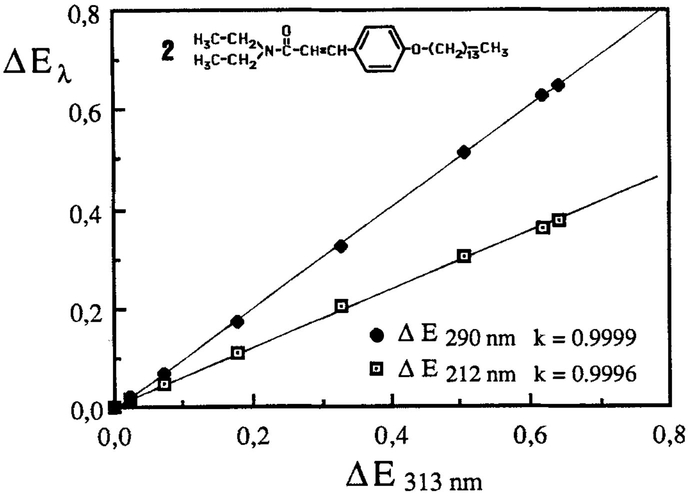


Figure 3. Extinction difference diagram ($\Delta E_{290\,nm}/\Delta E_{313\,nm}$; $\Delta E_{212\,nm}/\Delta E_{313\,nm}$) of short time irradiated *N*-diethyl-cinnamide 2 in cyclohexane ($c = 6 \times 10^{-5}$ mol/l).

band at 202 nm appears, due to the formation of the Z isomer. The Z isomer exhibits smaller extinction coefficients than the E isomer, and the absorption band, which was initially located at 282 nm, is shifted to shorter wavelengths. The findings, that the spectral changes given in figure 2 are due to the isomerization process, were also established by means of ^{1}H NMR. In these spectra, only signals which can be ascribed to the Z isomer formed upon short irradiation periods were found.

Extinction difference diagrams offer some information about the uniformity of a photoreaction [28]. The analysis, performed for model cinnamide **2** (see figure 3), demonstrates that the initial fast isomerization process is uniform, as indicated from the good correlation coefficients. Parallel proceeding photoreactions, in particular the bimolecular photocycloaddition, do not play a significant role, due to their appreciable lower quantum yields at these low concentrations. This was established for all the cinnamates investigated here. Extinction difference-correlation coefficients of multifunctional hexacyclen **1**, however, are worse than those obtained for monofunctional model compound **2**.

2.1.2. *Photodimerization*

Further irradiation causes the disappearance of the isosbestic points, and the system leaves the quasistationary state. This can be seen in the UV spectra of hexacyclen **1**, given in figure 4, where the absorption bands of the E and Z isomer are decreased continuously at approximately 300 nm. Furthermore, a new isosbestic point appears at 210 nm after 15 s of irradiation. The extinction difference analysis performed for the respective slow photoprocess (irradiation time $t > 15$ s) is given in figure 5. The plot shows a satisfying correlation only if we take into account the decreasing absorptions between 270 nm and 340 nm (e.g. $\Delta E_{300\,nm}/\Delta E_{313\,nm}$). The correlation of the extinction difference plots is worse, however, in the absorption region between 205 nm and 250 nm (e.g. $\Delta E_{205\,nm}/\Delta E_{313\,nm}$). This illustrates that the (2+2)-photocycloaddition reaction is not the only event contributing to the slow photoprocess. In addition, FT-IR and GPC investigations, which will be discussed later, demonstrate

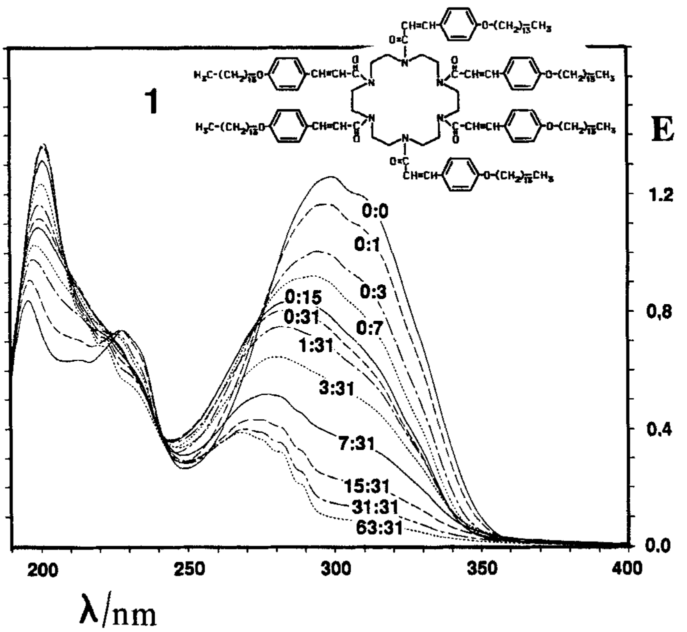


Figure 4. UV absorption spectra of irradiated hexacyclen **1** in cyclohexane ($c = 10^{-5}$ mol/l); irradiation time in minutes: seconds.

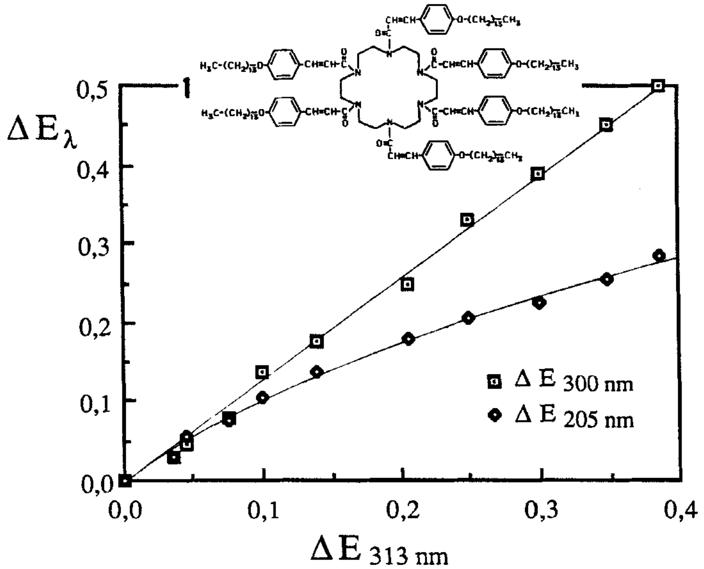


Figure 5. Extinction difference diagram ($\Delta E_{300\,\mathrm{nm}}/\Delta E_{313\,\mathrm{nm}}$; $\Delta E_{205\,\mathrm{nm}}/\Delta E_{313\,\mathrm{nm}}$) of irradiated hexacyclen **1** in cyclohexane ($c = 10^{-5}$ mol/l).

that side reactions occur under certain conditions. In this respect, the presence of air showed a marked influence on the distribution of the photoproducts.

An amazing result was obtained when comparing the efficiencies of the (2+2)-photocycloaddition of monofunctional diethyl-cinnamide **2** (6×10^{-5} mol/l) and hexacyclen **1** (10^{-5} mol/l) in cyclohexane. In order to rule out the influence of different chromophor concentrations, each solution was adjusted according to the number of chromophores and not to the number of molecules. Within the course of these investigations several mathematical approximations ($E=f(t)$) were employed to give a quantitative description of the photocycloaddition reaction. Experimental UV data for cinnamide **2** are approximated in a satisfying manner by

$$E=f(t)=A\exp(-ct)+D, \tag{1}$$

with the method of non-linear regression [29]. Furthermore, this equation fits the kinetics of the photocycloaddition of monofunctional compounds **3** and **4**. The non-linear correlation coefficients (R^2) obtained for compounds **2** and **3** are 0·9996. In figure 6, the experimental and calculated data are shown for diethyl-cinnamide **2**. In contrast to the analysis for model compounds **2**, **3**, and **4**, a parameter t^B defined by

$$E=f(t)=At^B\exp(-ct)+D \tag{2}$$

is introduced to describe the photokinetic behaviour of multifunctional hexacyclen **1**. This mathematical term takes into consideration that the photocycloaddition proceeds with a much higher quantum yield, a value, which is larger by a factor 50 than that obtained for model cinnamide **2**. Figure 7 compares the experimental data to the theoretically fitted curve using equation (2) ($R^2=0\cdot9890$). It could be argued that the much faster proceeding cycloaddition for multifunctional hexacyclen **1** is due to the close proximity of the photoreactive units, which leads to an effective *intramolecular* cycloaddition. However, the data given in figure 8, where the dependence of the quantum yield Φ on the concentration of hexacyclen **1** can be observed (Φ increases with c^2), clearly demonstrate the bimolecular nature of the respective reaction and support an *intermolecular* mechanism. These data were obtained by plotting the decreasing absorption at λ of 313 nm (beginning at the onset of the photostationary state) versus the irradiation time, and, by subsequent extrapolation to zero time. The fact that they do not correlate perfectly may be due to (i) aggregation phenomena [14], which are not linearly dependent on the concentration; (ii) errors in adjusting the

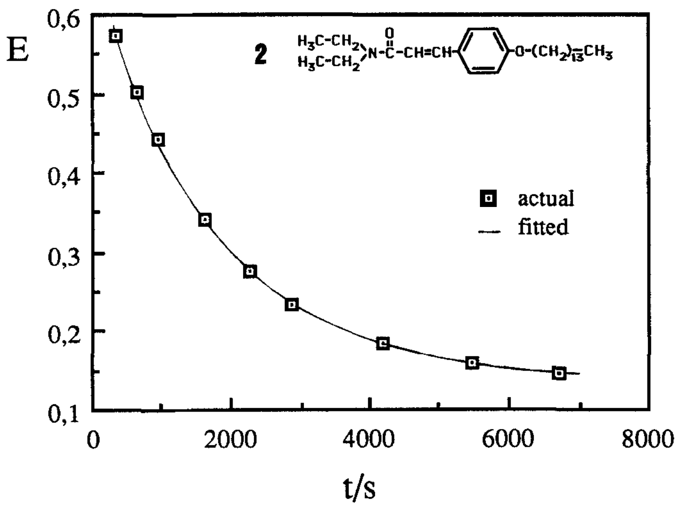


Figure 6. Photocycloaddition of *N*-diethyl-cinnamide **2** in cyclohexane ($c=6\times10^{-5}$ mol/l); experimental UV and fitted data according to equation (1).

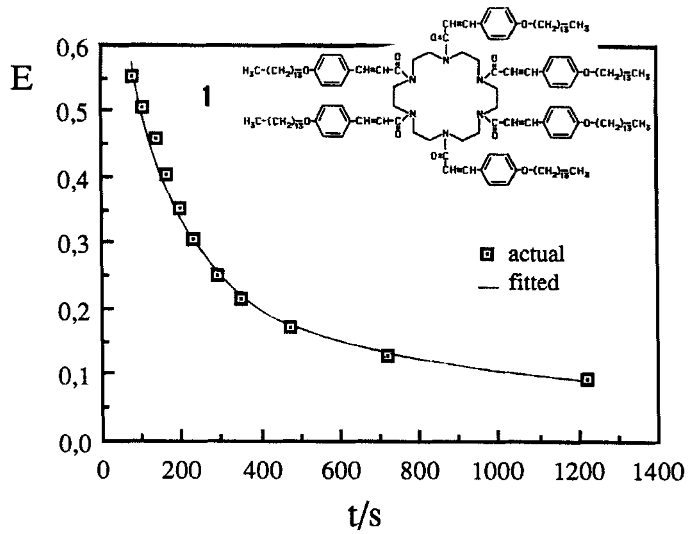


Figure 7. Photocycloaddition of hexacyclen **1** in cyclohexane ($c = 10^{-5}$ mol/l); experimental UV and fitted datas according to equation (2).

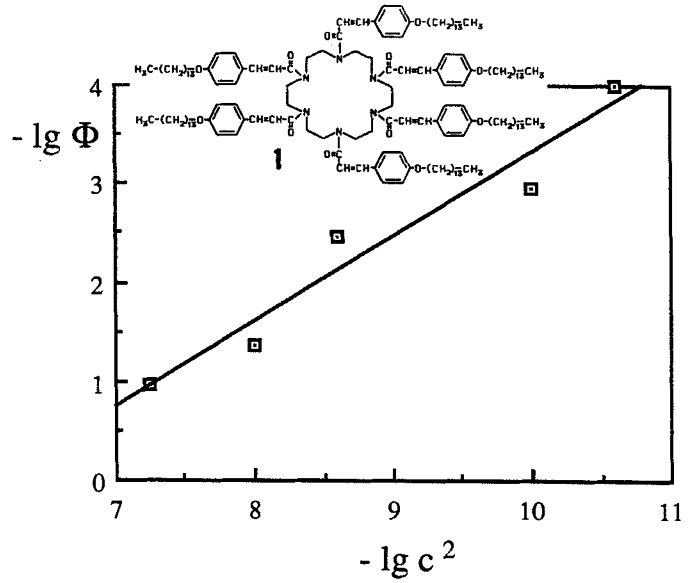


Figure 8. Photocycloaddition of hexacyclen **1** in cyclohexane; quantum yield, Φ, as a function of the concentration *c*.

concentration of the solutions; (iii) varying convection, due to the use of different cuvettes. Moreover, GPC investigations clearly indicate the formation of well-defined oligomeric photoproducts via an *intermolecular* reaction. Within the course of these investigations it was elucidated that 2–20 monomeric units were crosslinked within 40 min, when irradiating solutions of hexacyclen **1** in cyclohexane (10^{-4} mol/l). In figure 9 the UV light induced conversion of this system is plotted against the irradiation time. The conversion was determined according to the decreasing absorption at 310 nm. The plot shows the disappearance of the unsaturated C=C bonds to be an

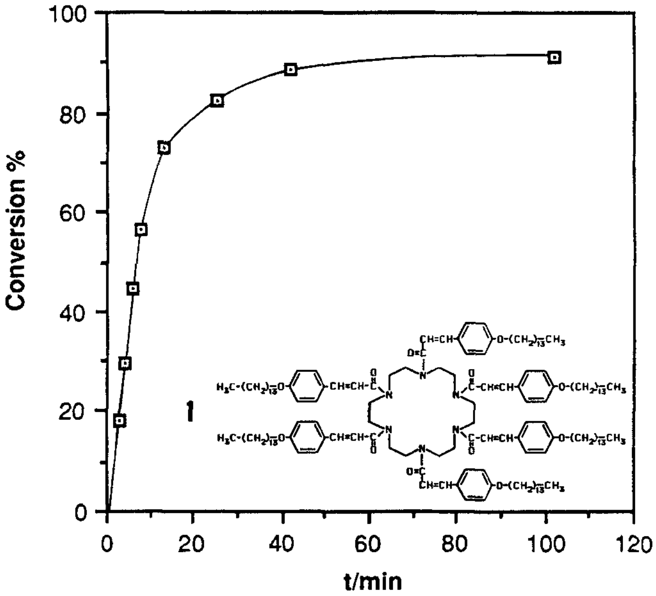


Figure 9. Photoconversion of irradiated hexacyclen **1** in cyclohexane ($c = 10^{-4}$ mol/l); determination via the degreasing absorption at 310 nm.

almost linear process up to 75 per cent conversion. The corresponding GPC diagram, which is given in figure 10, illustrates the molecular weight distributions of the photoproducts within the first 12·5 min of irradiation.

Depending upon the irradiation time, peaks appear, which were assigned to dimeric, trimeric, tetrameric, etc. structures. The calculated molecular weight for monomeric hexacyclen **1** is 2340 daltons. This value correlated well with the value obtained by GPC analysis (M_w at the peak maximum ~2700). After an irradiation period of 4 min, for example, a dimer (M_w ~4600) is the predominating photoproduct (conversion 20 per cent), with a small quantity of trimer (M_w ~6200) also present. By continued photolysis, these peaks are shifted towards higher molecular weights, whereby the new maximum is located at M_w ~ 8000, which corresponds to a tetrameric structure. Moreover, macromolecules with a high molecular weight and a broad distribution are formed (M_w ~ 10^5–10^6). At this stage nearly 85 per cent of the double bonds have reacted. Conversion of the remaining 15 per cent proceeds with a much lower quantum yield and leads mostly to high molecular weight branched polymers. Finally, after 205 min, the solution becomes turbid. Presumably, this is due to the formation of crosslinked insoluble photoproducts.

Totally different results were obtained when the photolysis experiment was performed in a good solvent (chloroform). Whereas no significant difference appears in the UV spectra, the GPC elution diagram, as given in figure 11, shows no formation of oligomeric photoproducts. In this case, even when approximately 80 per cent of the photoconvertable bonds have reacted, besides the monomer peak (M_w ~2700), only peaks which correspond to molecular weights smaller than the monomeric compound ($M_w < 1000$) were detected.

As an explanation for the results obtained from GPC, UV and kinetic investigations of hexacyclen **1** and model cinnamide **2**, the formation of columnar aggregates in the non-polar, poor solvent (cyclohexane) is suggested. This means that the disc-shaped,

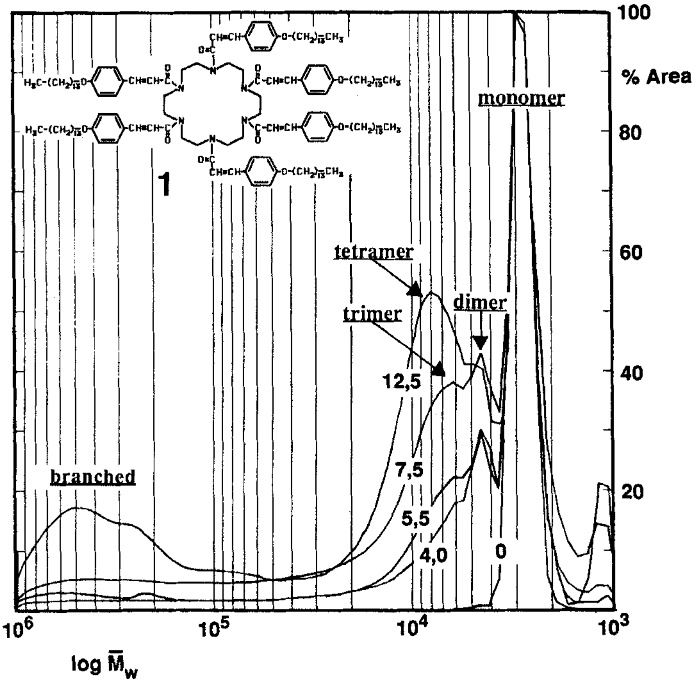


Figure 10. GPC elution diagrams of irradiated hexacyclen 1 in cyclohexane ($c = 10^{-4}$ mol/l); molecular weight distribution as a function of the irradiation time; irradiation time in minutes.

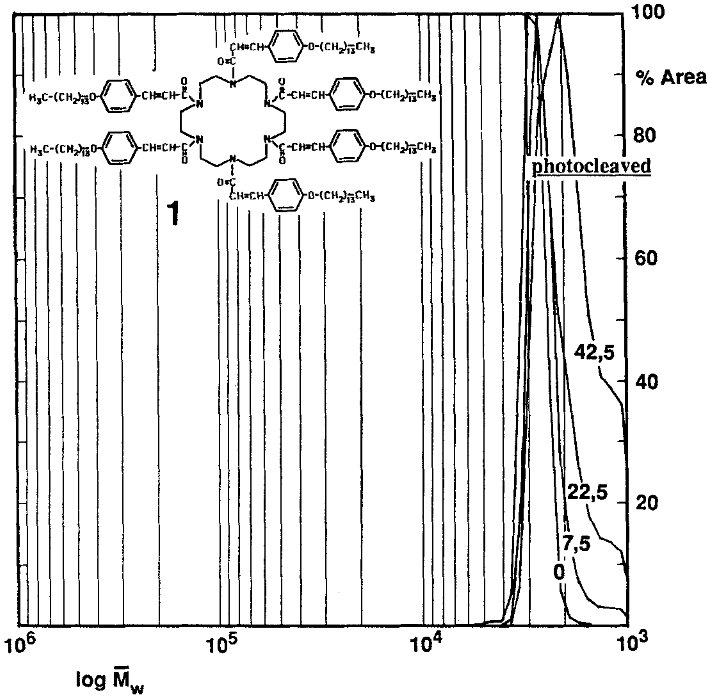
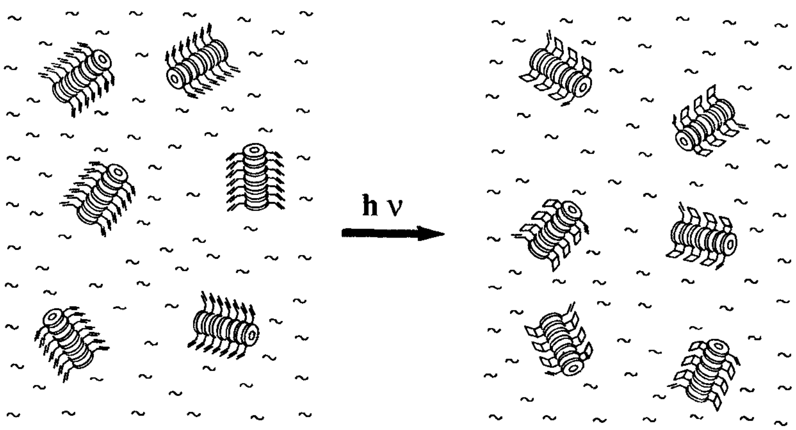


Figure 11. GPC elution diagrams of irradiated hexacyclen 1 in chloroform ($c = 10^{-4}$ mol/l); molecular weight distribution as a function of the irradiation time; irradiation time in minutes.



Scheme 5. Schematic representation of intracolumnar crosslinking in preformed aggregates of hexacyclen **1** in cyclohexane.

amphiphilic molecules are stacked in piles, with their short axes parallel to one another. This leads to a columnar structure with a hydrophobic periphery and a hydrophilic interior, thus allowing for *intermolecular* cycloaddition between adjacent molecules in the column (scheme 5). It is probably the discoidal, amphiphilic structure of hexacyclen **1**, exhibiting a hydrophilic core and a hydrophobic periphery, which may predestinate the molecule to form columnar aggregates in a non-polar solvent. This could explain the much higher efficiency of the (2+2)-photocycloaddition of hexacyclen **1** in comparison to the monofunctional model cinnamide **2**. Light scattering and fluorescence spectroscopic measurements are currently under investigation in order to elucidate the proposed aggregation. The results obtained in a good solvent (chloroform) can be interpreted in terms of photocleavage and interactions with the solvent. Moreover, an intramolecular photocycloaddition of the adjacent cinnamoyl chromophores within one molecule is obvious, because a peak equivalent to the molecular weight of the monomer is still present even after exhaustive irradiation (see figure 11). The intramolecular process for hexacyclen **1** is possible, due to its multifunctional character. This is not inconsistent with the observations of Frings *et al.* [30], who detected no photodimer when they performed the photolysis of trans-ethyl-cinnamate in chlorine containing solvents. Indeed, no trace of dimer was detected, when the photolysis was carried out with monofunctional diethyl-cinnamide **2**. Furthermore, the authors [30] concluded by fluorescence measurements and flash photolysis that singlet excitated cinnamates and chlorinated solvent molecules form exciplexes with a charge transfer character.

Further investigations of the quantum yield dependence on the type of solvent used were carried out in order to prove any of the aggregation phenomena suggested here. In accord with this hypothesis, quantum yields Φ for compounds **1** and **2** are generally smaller in chloroform than in cyclohexane. Replacing chloroform by another polar, in this case, protic solvent (*n*-butanol), Φ of the (2+2)-photocycloaddition of hexacyclen **1** is smaller by a factor 3·4 than for the apolar cyclohexane. As a further spectroscopic method, FT-IR spectroscopy was applied to the present photoreactive systems. Figure 12, for example, gives the spectra of compound **2** in cyclohexane prior and subsequent to irradiation. The FT-IR spectra clearly demonstrate the disappearance of the characteristic deformation mode of the cinnamoyl moiety at 980 cm^{-1}. Besides this,

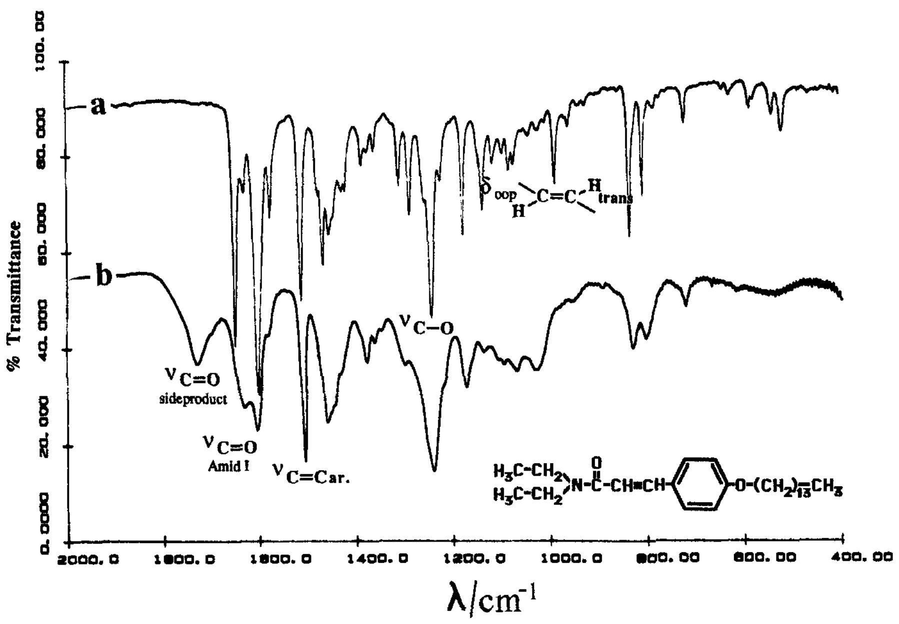


Figure 12. FT-IR spectra of *N*-diethyl-cinnamide **2** in cyclohexane ($c = 6 \times 10^{-4}$ mol/l); (*a*) prior and (*b*) after exhaustive irradiation as indicated by the vanished absorption at 300 nm.

a new absorption band located at 1730 cm^{-1} appears. The appearance of this IR band in the carbonyl absorption region is also observed with several samples of hexacyclen **1**, independently of the solvent used. Either oxygen [31], or autooxidation to benzaldehyd [18, 21] may play a role in the formation of the side product. The former mechanism is likely, since the intensity of the carbonyl absorption band is dependent on the content of air dissolved in the solution. Indeed, the carbonyl absorption of the side product is considerably reduced if the solution is purged with argon prior to irradiation.

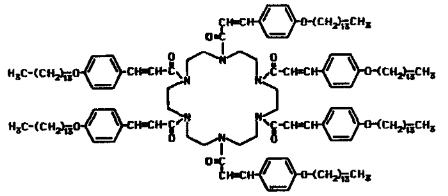
The formation of any carbonyl side product requires cleavage of the amide bond [32]. For hexacyclen **1**, this results in a tremendous reduction of its initial molecular weight. This is confirmed by GPC analysis, which demonstrates that purging a solution of hexacyclen **1** in cyclohexane with argon considerably reduces the formation of cleaved photoproducts. Furthermore, no high molecular weight branched polymers have been detected in purged solutions. These results, together with the findings that the quantum yields of purged solutions are smaller, suggests that radical cleavage and crosslinking reactions via oxygen are participating in the photolysis of air containing solutions.

Upon irradiation of model cinnamide **2** in cyclohexane, a trace of a dimeric cycloaddition product is formed. In chloroform, however, under the same conditions, no further peaks appear in the GPC diagram except for the peak in the molecular weight range, which is equivalent to the starting material prior to irradiation. In contrast to hexacyclen **1**, no cleaved photoproduct is detectable for monofunctional cinnamide **2**, due to insufficient resolution of the separation column used in GPC. The molecular weight of any cleaved photoproduct has to be in the range of the starting material prior to irradiation.

2.2. *Photoreactions in spin coated, amorphous films*

Spin coated films of hexacyclen 1 were annealed at 70°C subsequent to the spin coating procedure in order to remove small amounts of remaining solvent (toluene). These films are highly photoreactive, since a conversion of 100 per cent upon irradiation can be obtained within a reasonable time scale. Figure 13 shows the UV spectra of hexacyclene 1 spin coated on quartz, irradiation was carried out at room temperature. The photolysis (see figure 13) appears extremely uniform and a quasistationary state of the E/Z-isomerization is not visible, as would be indicated by a shift of the most intensive absorption bands towards shorter wavelengths (see figure 4). The absorption bands at 300 and 225 nm decrease, and another absorption band at 198 nm appears successively. However, extinction difference-analysis demonstrates that two different time scale processes are contributing to the photolysis. These two processes, a fast (irradiation time $t < 300$ s) and a subsequent slower one ($t > 300$ s), are spectroscopically uniform, as indicated by their non-linear correlation coefficients ($R^2_{\text{fast}} = 0{\cdot}9992$; $R^2_{\text{slow}} = 0{\cdot}9999$). The decreasing extinction ($E = f(t)$) can also be approximated by equation (2). The graphic representation is shown in figure 14. The irradiated films are completely soluble in chloroform, even those with a 90 per cent photoconversion. No trace of dimer, further oligomers, and branched polymers was detected in the GPC elution diagram. The molecular weight of the photoproduct is

1



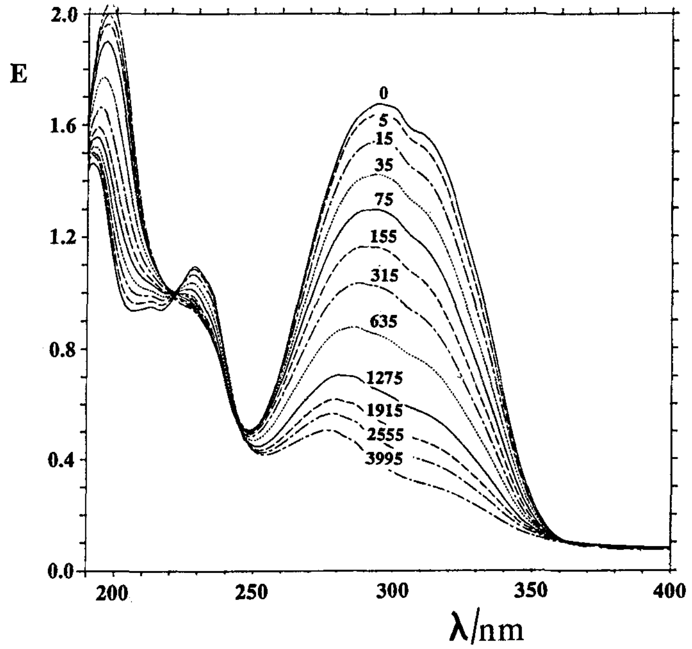


Figure 13. UV absorption spectra of irradiated hexacyclen 1 spin coated on quartz; irradiation time in seconds.

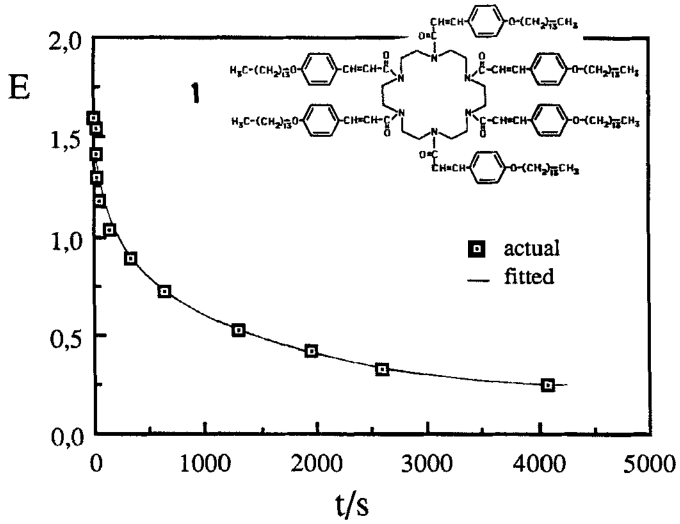


Figure 14. Photoreaction of hexacyclen 1, spin coated on quartz; experimental UV and fitted data according to equation (2).

identical to that of the starting material **1**. These results point toward an effective intramolecular photocycloaddition between the adjacent chromophores in addition to the preceding E/Z-isomerization, which is responsible for the initial fast process ($t < 300$ s). However, an intermolecular photocrosslinking does not occur.

2.3. *Photoreactions in the mesophase*

UV spectra of hexacyclen **1** in its isotropic melt resemble those recorded in dilute solution and in the amorphous, spin coated state. The absorption maxima are located at 313 nm and 295 nm. This suggests that the same type of randomness exists in the orientation of the chromophores. In contrast to this, UV spectra of those samples, which were prepared as a thin film between two quartz slides, either in the mesophase at elevated temperatures or by subsequent quenching into the supercooled liquid-crystalline state, are quite different and depend on their thermal history. The observed broadening of the absorption band in the 300 nm region together with a decreased extinction may be due to aggregation or macroscopic orientation of the chromophores. Intermolecular interactions in the ordered environment lead to shifts and splittings of absorption bands as a consequence of exciton splitting.

When a thin film of hexacyclen **1**, prepared either between quartz slides or via spin coating on quartz, is irradiated in its mesophase (220°C), the birefringent texture disappears after 1 min. Moreover, for the spin coated film, tiny droplets of an isotropic melt can be observed. In the UV spectrum of a chloroform solution, prepared by dissolving the irradiated film, a shift of the absorption maximum, together with a decreased extinction, can be observed. This feature is characteristic of the initial E/Z-photoisomerization (see figure 4). According to these observations, E/Z-isomerization of the cinnamic acid moieties is responsible for the photochemically triggered transition from the mesophase into the isotropic melt [27]. A small quantity of cinnamoyl groups changes their geometrical shape, hence destroying the mesomorphic order. In the present case, as a consequence of the fast photoisomerization at elevated temperatures, the columnar order vanishes and continued irradiation leads mainly to an undefined polymeric network with high molecular weights, cleaved photoproducts, and only traces of oligomers. Thus, the photoisomerization competes with the photocycloaddition in order to obtain defined intracolumnar crosslinked aggregates.

2.4. *Photoreactions in the supercooled mesophase*

Similar to liquid-crystalline polymers with T_g above room temperature, the columnar order within the mesophase of hexacyclen **1** can be frozen in a glassy state. According to DSC, temperature dependent X-ray investigations and polarizing microscopic observations, its crystal to mesophase transition (T_{CD}) is located at 217°C [6]. When annealing a sample of hexacyclen **1** at a temperature just below T_{CD}, recrystallization occurs immediately. However, the birefringent texture of its mesomorphic columnar state can be frozen in by simply quenching the sample, as revealed by X-ray investigations [6]. The texture of a thin film prepared in this manner does not change, when observing the sample after storage at room temperature for several hours; this indicates the stability of the supercooled discotic state.

Spectral investigations demonstrate that E/Z-photoisomerization is also present in the supercooled mesophase of thin films prepared between quartz slides. However, in contrast to the photolysis in the mesomorphic range (220°C), the birefringent texture is stable for 50 min upon continued irradiation. In the respective GPC diagram, as given in figure 15, several sharp peaks appear which were assigned to a dimer and trimer. Actually, the peak positions are the same as those observed in the GPC diagram of hexacyclen **1** irradiated in cyclohexane (see figure 10). However, the peak areas of the oligomeric fractions are smaller and do not increase, even after long irradiation. After 200 min the photoconversion reaches a limit, and continued irradiation up to 560 min

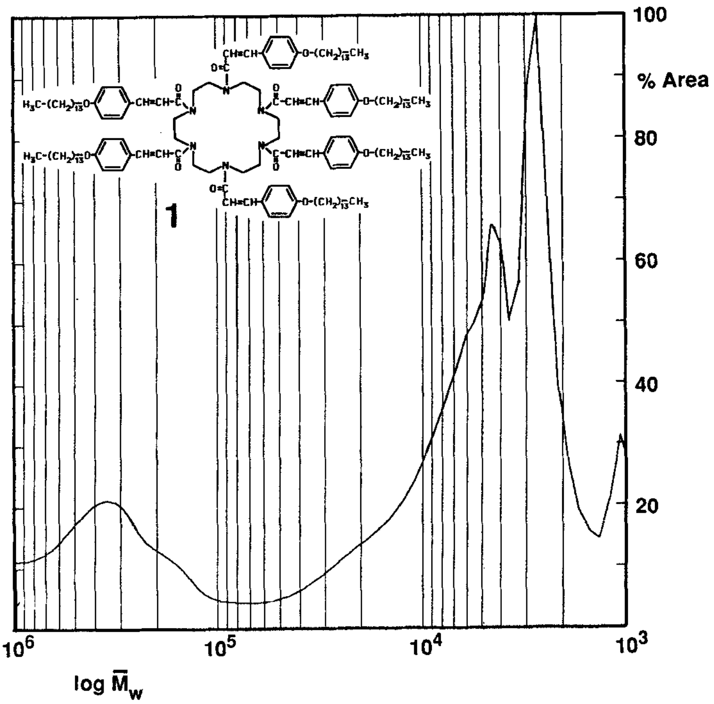


Figure 15. GPC elution diagram of irradiated hexacyclen **1** in its supercooled mesophorphic state; irradiation time 45 min; thin film prepared between quartz slides.

does not change the absorption at all. At this state, the remaining double bonds are not able to react further. Approximately 25 per cent of the irradiated sample remains on the front quartz slide, oriented towards the light source, as a highly branched polymer insoluble in chloroform and DMSO. However, the insoluble film is photoreactive again afterwards, presumably due to swelling and hence the induction of an increased mobility of the reactive sites within the branched polymer. Whereas the restricted mobility of the photoconvertible cinnamate moieties in the supercooled film reduces the competing isomerization, photocycloaddition stops before all double-bonds are converted quantitatively [22].

Similar behaviour is shown by a spin coated film in its supercooled discotic state. This sample was annealed for 90 min at 220°C prior to quenching, preventing any contact with light and air. A very regular texture with small domains can be observed with a polarizing microscope. In these films E/Z-isomerization is suggested to take place as a thermally induced reaction. Figure 16 shows that the UV spectrum recorded prior to annealing is changed by the annealing procedure in a way similar to the changes induced by short time UV irradiation of dissolved hexacyclen **1** (see figure 4). On subsequent irradiation, the photostationary state is approached now from the opposite direction, i.e. Z/E. The thermally induced increase in the population of the Z-isomer now decreases, due to the influence of UV light. This was deduced from UV spectroscopic investigations, as shown in figure 17, where the absorption in the 300 nm region is slightly shifted to longer wavelengths. The photochemical behaviour of these

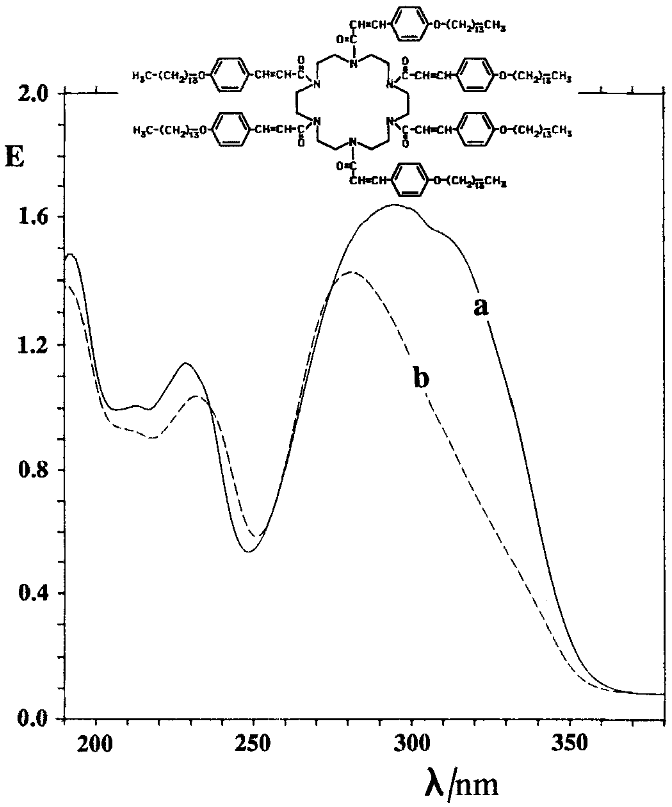


Figure 16. UV absorption spectra of hexacyclen **1**; (*a*) spin coated on quartz and (*b*) subsequently annealed at 220°C for 90 min.

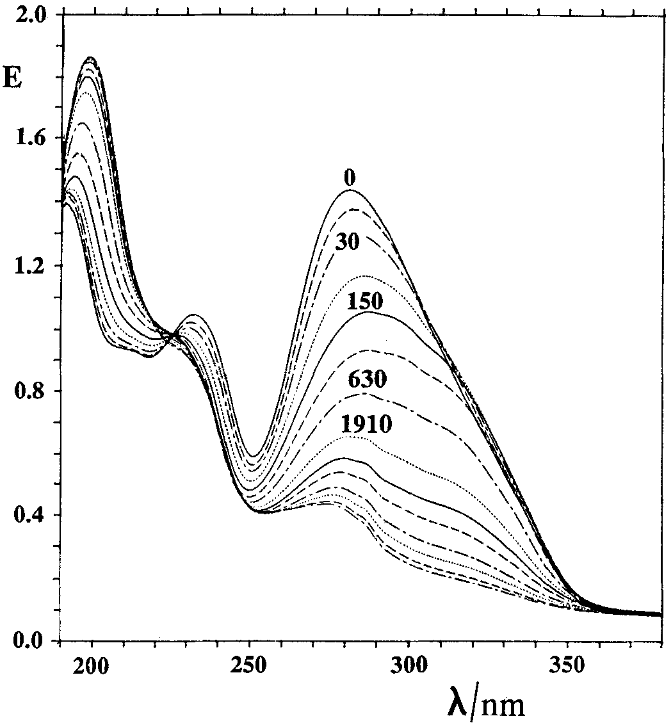


Figure 17. UV absorption spectra of irradiated hexacyclen **1** spin coated on quartz and subsequently annealed at 220°C for 90 min; irradiation time in seconds.

films, exhibited on further irradiation, is quite similar to that observed in the amorphous film. Again, two time scale processes are contributing to the photolysis (fast $t < 300$ s; slow $t > 300$ s). Both are spectroscopically uniform as indicated by their large non-linear correlation coefficients ($R^2_{\mathrm{fast}} = 0{\cdot}9969$; $R^2_{\mathrm{slow}} = 0{\cdot}9999$). However, Φ is smaller by a factor 10 in this case.

At the stage of complete photoconversion of the cinnamoyl moieties, only small amounts of dimeric and other oligomeric products were detected. The main product also seems to be an intramolecular crosslinked molecule. Further, the excellent solubility of the irradiated film in chloroform suggests that the main photoproduct is not a high molecular weight branched polymer. Spin coated films are highly photoreactive up to high conversions. These findings may be due to the increased mobility of the cinnamoyl groups caused by traces of remaining solvent (toluene), which is used in the spin coating procedure.

3. Conclusions

The photochemical behaviour of liquid-crystalline hexa-cinnamoyl substituted hexacyclen **1** and of different monofunctional model compounds was investigated in solution and in bulk by UV, FT-IR, ^{1}H NMR spectroscopy and GPC analysis. It could be shown that the photochemistry of the cinnamoyl chromophores is determined by the competition between (2 + 2)-photocycloaddition, E/Z-photoisomerization and, in the presence of air, a further, not yet clearly identified side reaction. Upon irradiation, the isomerization rapidly leads to a quasistationary state between the E- and the Z-isomer. Continued irradiation causes photocycloaddition to proceed as a parallel event, either as an intramolecular or an intermolecular process.

In cyclohexane, a poor solvent, it is suggested that self-aggregation of amphiphilic hexacyclen **1** leads to columnar aggregates, which upon irradiation undergo intracolumnar photocycloaddition between the photoreactive sites of the adjacent molecules. Thus, depending on the irradiation time and further reaction conditions, oligomers are formed consisting of 2–20 molecules bound to one another in a tube-like array. Experiments to verify the geometrical shape of these photoproducts are currently under investigation. The high quantum yield of the photocycloaddition reaction of hexacyclen **1** in cyclohexane supports this hypothesis. In chloroform, a good solvent, aggregation is prevented and the photolysis primarily results in cleaved photoproducts and intramolecular dimerized cinnamoyl chromophores.

Irradiation in the columnar mesophase at 220°C immediately destroys the liquid-crystalline order, due to E/Z-photoisomerization. Continued irradiation of the isotropic melt, thus obtained, yields only high molecular weight crosslinked products. The restricted mobility of the chromophores in the supercooled films at room temperature reduces the order destabilizing effect of the E/Z-photoisomerization. On the other hand, the restricted mobility and the changed reactive sites of the cinnamoyl groups reduces the quantum yield of the intermolecular photocycloaddition. In these experiments only small amounts of dimeric and oligomeric photoproducts were detected. In the spin coated amorphous film the photoreaction proceeds with a high spectroscopical uniformity, but without any intermolecular photocycloaddition.

Obviously, a controlled photocycloaddition of hexacyclen-hexa-cinnamate **1** in order to synthesize covalently bound supramolecular assemblies can be realized more favourably in poor solvent than in the ordered bulk state. According to the results obtained, photoisomerization does not disturb the arrangement of the pre-associated assemblies. Further, a fluid-like environment is present, which provides the required population of reactive sites, leading to effective photodimerization. These results demonstrate that the photochemical behaviour of cinnamoyl substituted hexacyclen is strongly influenced by its ability to self-organize, either due to its anistropy in shape or to its amphiphilic structure. The competition between different photochemical reaction pathways, the quantum yields and the ratio between intra and intermolecular photocycloaddition is determined by order, compartmentilization and specific dynamics within the sample. On the other hand, the liquid-crystalline order of the system is influenced by the photoreaction. Photoreactions in organized systems can be a useful tool not only to synthesize polymeric supramolecular assemblies, but also to probe the micromorphology of such systems.

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